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AN XPS EXAMINATION OF CATALYST MB-VA-FI FOLLOWING CALCINATION AT 450° and 1000°C: VARIATION IN SURFACE CHEMISTRY

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XPS study completed for Dr. V. Allenger

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ABSTRACT

The surface composition and surface chemistry of an alumina supported fluorine containing catalyst was determined by X-Ray Photoelectron Spectroscopy (XPS). After preparation, some of the catalyst extrudate pellets were calcined for 6 hours at 450°C, the remainder at 1000°C. Major differences in the F/Al ratio were observed, indicating that the high calcination temperature had caused nearly complete removal of fluorine from the catalyst. Thus, this particular F-alumina catalyst should be used only at relatively low temperatures (much less than 1000°C and probably less than 450°C); otherwise it will decompose causing a shortened life time, and a rapidly decreasing feedstock conversion rate with unacceptable fluorine emissions.

RÉSUMÉ

La nature chimique de la surface d'un catalyseur de fluor supporté sur de l'alumina a été établie par la spectroscopie photoélectronique à rayons-X (XPS). Après leur préparation, deux échantillons du catalyseur ont été calcinés pendant six heures, l'un à une température de 450°C, l'autre à 1000°C. Une importante différence a été observée dans le rapport des concentrations entre les deux échantillons. L'analyse de l'échantillon soumis à la température de calcination la plus élevée a établie la disparition presque totale du fluor de la surface du catalyseur. Si l'efficacité catalytique est proportionelle à la fraction F/Al, elle diminura rapidement aux températures élevées à cause de l'émission de fluor. La stabilité thermique du catalyseur en question limite cependant la température réactionelle à 450°C.

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INTRODUCTION

EXPERIMENTAL PROCEDURES AND INSTRUMENTATION

A. SAMPLE PREPARATION

An alumina supported fluoride containing catalyst, labelled MB-VA-FI, was prepared by the gel impregnation-method: an aqueous solution of ammonium fluoride was mixed with enough α alumina monohydrate (Catapal S.B.) to yield a F/Al ≈ 0.1

Sufficient nitric acid was then added to allow gel formation. The paste was passed through the extruder system, producing cylindrical pellets ≈ 10 mm by 4 mm in diameter. The pellets were dried for 7 hours at 110°C to remove moisture. After drying, the pellets were calcined for 6 hours; one portion at 450°C, the remainder at 1000°C.

These extrudate samples were then divided into 4 groups a) 450°C extrudate, b) 1000°C extrudate, c) 450°C extrudate after fine grinding, and d) 1000°C extrudate after fine grinding. The samples were then dried in an oven overnight at 100°C. The extrudate formed samples were analyzed "as is". The ground extrudates were pressed into KBr type discs (10 mm x 2 mm) using an IR die and hydraulic press. Each sample was then mounted on the specimen insert probe and evacuated to ≈ 10^{-6} torr in the preparation/pumpdown chamber.

B. INSTRUMENTATION

A combination x-ray photoelectron (XPS) and Auger electron spectrometer (AES) manufactured by Physical Electronics Division, Perkin-Elmer Corporation (PHI-548E) having depth profiling capability (Ar^+ 5KeV ion gun Model PHI-4303), specimen introduction and transfer fore-chamber (PHI-2100) and multiple-technique analytical computer system (MACS) was employed for this investigation. The base pressure of this instrument is ≈ 2 x 10^{-10} torr (ultra-high vacuum, UHV).

X-ray photoelectron spectroscopy (XPS) also called electron spectroscopy for chemical analysis (ESCA) and Auger electron spectroscopy (AES) are highly surface sensitive, direct and in many cases non-destructive. Both XPS and AES readily provide qualitative information (which elements are present), probing the outermost 1-5 nm region of a sample's surface. Using calibration techniques (element and instrument sensitivity factors), semi-quantitative and in some cases quantitative surface composition data is possible.

All elements, except hydrogen and helium can be detected with an ultimate sensitivity approaching 10^{-9} gm cm^{-2} of surface. Usually it is possible to confirm chemical environment (oxidation state, co-ordination number) of a surface sited element from XPS binding energies (chemical shift information).

Extensive reviews of XPS (1-5) theory and use are available. Details of the specifications and features of the PHI multi-technique XPS/AES instrument utilized in this study are available (6).

Each sample was placed on an introduction sample holder, mounted on the specimen insert probe and evacuated to ≈ 10^{-7} torr in the preparation forechamber. XPS analyses were performed at ≈ 10^{-9} torr in the analytical chamber using a dual Al/Mg anode equipped x-ray gun operating at 300 W (15 KeV x 20 mA) in the Mg kα mode. The resulting x-rays of energy ≈1254 eV were directed onto an ≈ 5 mm^2 area of the sample.

The quantity of electrons photoejected by x-rays (XPS) and their kinetic energies are monitored using a high resolution double pass cylindrical mirror electron energy analyzer (CMA) with a coaxially mounted electron gun and associated electronics. The entire analytical operation is computer controlled.A spectrum of peak intensity (electron counts) vs. binding energy is then plotted. Samples are normally examined using two XPS scanning modes:

(a) initial "surveying" for determining all elements present; and

(b) "multiplexing" specific regions of the survey at greater resolution for quantitative and/or chemical structure information

The XPS "survey technique" can identify elements present down to the minor element level by sweeping the binding energy scale (0 → 1254 eV) in 1 eV/100 microsecond increments using a CMA pass energy of 100 eV. Spectrum acquisition times for acceptable S/N level spectra is usually 15 minutes. For the "multiplex technique", ultimate resolution is achieved at lower pass energies,

typically 25 or 50 eV and binding energy windows of either 10, 20 or 40 eV depending on the complexity of an individual photoelectron line envelope and on the proximity of one peak to another. Acquisition times for multiplex spectra vary greatly depending on the element's surface concentration. The time required to give an acceptable S/N multiplex spectrum for elements present at the major and minor level are typically 5 minutes and 15 minutes respectively.

The carbon (C 1s) signal is used to determine the degree of specimen charging; an electron flood gun (specimen neutralizer) is used to greatly reduce charging of insulators and hence eliminate identification problems caused by differential charging (ghost) peaks. Thus all XPS photoelectron lines are referenced to the accepted hydrocarbon C 1s binding energy of 284.6 eV. Gold foil is used to calibrate the energy scale of the spectrometer (Au $4f_{7/2}$ = 83.8 eV).

DISCUSSION

Part 1 Catalyst MB-VA-FI (Calcined 450°C)

(a) Extrudate Form

The XPS surface analysis results are shown in Table 1 for the F-Al_2O_3 extrudates calcined at 450°C. The XPS survey spectrum (Figure 1) indicates the presence of Al,O,C,F and S. XPS multiplex spectra for these elements are shown in Figures 2-6.

Several points are noteworthy, for example, fluorine sited inorganically (ie AlF_3) is detected; nitrogen species are not detected; the Aluminum and oxygen peak binding energies and intensities are correct for Al_2O_3; sulphur as the sulphate anion is detected at the surface and the carbon present is ≈ 70% hydrocarbons with the remainder oxy-carbon species. The surface F/Al ratio experimentally found by XPS (0.1) is identical to that calculated for the bulk based on the starting material weights.

Wet chemical techniques to determine fluorine are slow and tedious with interference problems. The XPS method is direct, non-destructive and relatively quick with no interferences. Note the experimentally determined oxygen content (56.3 At.%) is in good agreement with that required for stoichiometric balance

(oxygen calculated 55.7 At.%) taking the Al content (33.5 At.%) as being due to Al_2O_3 and the sulphur (1.3 At.%) as being due to sulphate anions.

(b) Finely Ground Form

To determine the effect of calcination and/or the uniformity of the fluorine content with distance into the alumina, the extrudates "as received" were ground to a fine powder in a mortar and pestle.

The surface chemical composition of the ground catalyst was then determined by XPS (Table 2, figures 7-11).

The decrease in carbon content with respect to the extrudate form indicate much of the carbon species were deposited after the catalyst was prepared. Handling in air and vacuum pump oil contamination during introduction to the XPS spectrometer are indicated. The freshly ground catalyst surface did not have any sulphur present indicating "as received" extrudate had sorbed sulphate preferentially at the "as received" surface. The F/Al ratio was 0.16 (≈ 60% larger than in the extrudate specimen) indicating that F was not uniformly sited in the extrudate. Either diffusion of fluoride away from the surface into the bulk ocurred or fluorine anions were liberated from the extrudate causing a depleted surface zone. Heating to 450°C may have provided enough energy to break the Al-F bonds freeing fluorine as HF.

The thickness of this fluoride depletion zone is $\leq$ 50 Å based on the known estimated electron escape depth for F 1s. Temperature induced diffusion of fluoride into the alumina lattice is not likely, based on the results in Part 2 below. After heating to 1000°C, the fluoride concentration was reduced to 0.6 At.% and was essentially identical in the "as received" extrudate and the finely ground states.

Part 2 Catalyst MB-VA-FI (Calcined at 1000°C)

(a) Extrudate Form

The results of the XPS surface analysis of the catalyst calcined at 1000°C are shown in Table 3, Figures 12-17.

The F/Al ratio (0.02) now is greatly reduced compared to the 450°C calcined catalyst. No S or N species are detected, however silicon (ie silica) and carbon contents are much larger than in the 450°C exposed catalyst.

The surface sited Si and C are probably contaminants deposited from the 1000°C heating in the muffle furnace (ie ceramic elements and/or insulation).

The oxygen content measured directly by XPS (51.6 At.%) is in excellent agreement with that required for the postulated species SiO_2 and Al_2O_3 (51.7 At.%).

(b) Finely Ground Form

The surface chemical composition of the extrudate catalyst calcined at 1000°C then powdered is shown in Table 4, (see figures 18-22). The F/Al ratio (0.023) is essentially unchanged with respect to the "as received" extrudate calcined at 1000°C; fluoride added in the preparation has been almost eliminated after the 1000°C calcining treatment.

Both the C and Si present on the as received extrudate surface were greatly reduced after grinding; the silicon was not detected while the carbon has been halved indicating their preferential surface siting and further supporting the claim that the muffle furnace was the main source of these contaminents. A small amount of Ti (0.2 At.%) was detected after grinding the extrudate however its chemistry and source are not apparent. The catalyst was experimentally found tocontain 55 At.% oxygen; a stoichiometric material balance calculation assuming the presence of Al_2O_3 (35.2 At.% Al experimentally determined) yields 52.8 At.% oxygen in reasonable agreement with the analysis. The other 2 At.% oxygen is sited as oxy-carbon species as seen from the C 1s spectrum (Figure 20).

SUMMARY

The surface region of this fluorine-alumina catalyst (MB-VA-FI) calcined at 450°C has a F/Al ratio of 0.1 identical with the expected ratio as calculated from the weights of starting reagents used.

These extrudate pellets were then finely ground and re-examined by XPS to determine how the composition varied between the interior (bulk) and the surface. The F/Al ratio for the ground catalyst increased to ≈ 0.16, probably indicative that the surface region was fluorine depleted due to the 450°C calcine treatment. Loss of fluorine in the surface region (as HF) is most likely. The fluorine remaining sited in the catalyst is an inorganic fluoride species probably AlF_6^{3-} or the compound AlF_3.

The surface (extrudate) and the interior (ground) F/Al ratio was ≈ 0.02 and ≈ 0.023 respectively for the catalyst calcined at 1000°C. Thus the increase from 450°C has volatilized essentially all the fluoride (probably as HF). This XPS study clearly indicated the siting of fluoride in the alumina, the amount and its instability at elevated temperatures (> 400°C). XPS is shown here to be a relatively rapid, non destructive, and reliable qualitative and semi-quantitative tool in chemically analyzing for fluorine, an element very difficult to measure by any other technique. In this study, XPS has also been found to provide chemical composition information (at the minor and major element level) comparable to "bulk" spectroscopic techniques such as the electron microprobe or X-ray fluorescence. XPS additionally permits rapid bulk versus surface composition analysis due to its extremely high surface selectivity and sensitivity.

REFERENCES

1. Carlson, T.A. Photoelectron and Auger Spectroscopy, Plenum, New York, N.Y.; 1975.

2. Brundle, C.R. and Baker, A.D. (editors) Electron Spectroscopy: Theory, Techniques and Applications, Vol. 1, 2, 3; Academic Press, New York, N.Y.; 1979.

3. Windawi, H. and Ho, F.F.L. Applied Electron Spectroscopy for Chemical Analysis; Vol. 63, in "Chemical Analysis", Elving, P.J. and Winefordner, J.D. (editors); Wiley-Interscience, New York, N.Y.; 1982.

4. Hercules, D.M. Electron Spectroscopy, Analytical Chemistry, 42, 20A-40A; 1976.

5. Bancroft, G.M., Brown, J.R. and Fyfe, W.S. Advances In, and Applications of, X-Ray Photoelectron Spectroscopy (ESCA) in Mineralogy and Geochemistry, Chemical Geology, 25, 227-243; 1979.

6. Palmberg, P.W. A Combined ESCA and Auger Spectrometer, J. Vac. Sci. Technol., 12, 379-384; 1975.

TABLE I

CATALYST MB-VA-FI (CALCINED - 450°C) AS RECEIVED

Element	XPS		Bulk (Wt.%) (±5%)	Remarks
	At. % (±10%)	Wt. %		
Al	33.5	45.7		- Al_2O_3
O	56.3	45.5		
C	5.7	3.5		70% $(CH_3)_2$, 20% C-O, 10% C=O
F	3.3	3.2		- inorganic form (ie AlF_3)
S	1.3	2.1		- sulphate, no sulphide.
				Note: F/Al = 0.10 No N present.

TABLE 2

CATALYST MB-VA-FI (CALCINED - 450°C) FINELY GROUND

Element	XPS		Bulk (Wt.%) (±5%)	Remarks
	At. % (±10%)	Wt. %		
Al	33.0	46.5		- Al_2O_3
O	55.5	44.7		
C	6.2	3.7		
F	5.3	5.1		- inorganic form
				Note: 1. No S or N measured. F/Al = 0.16

TABLE 3

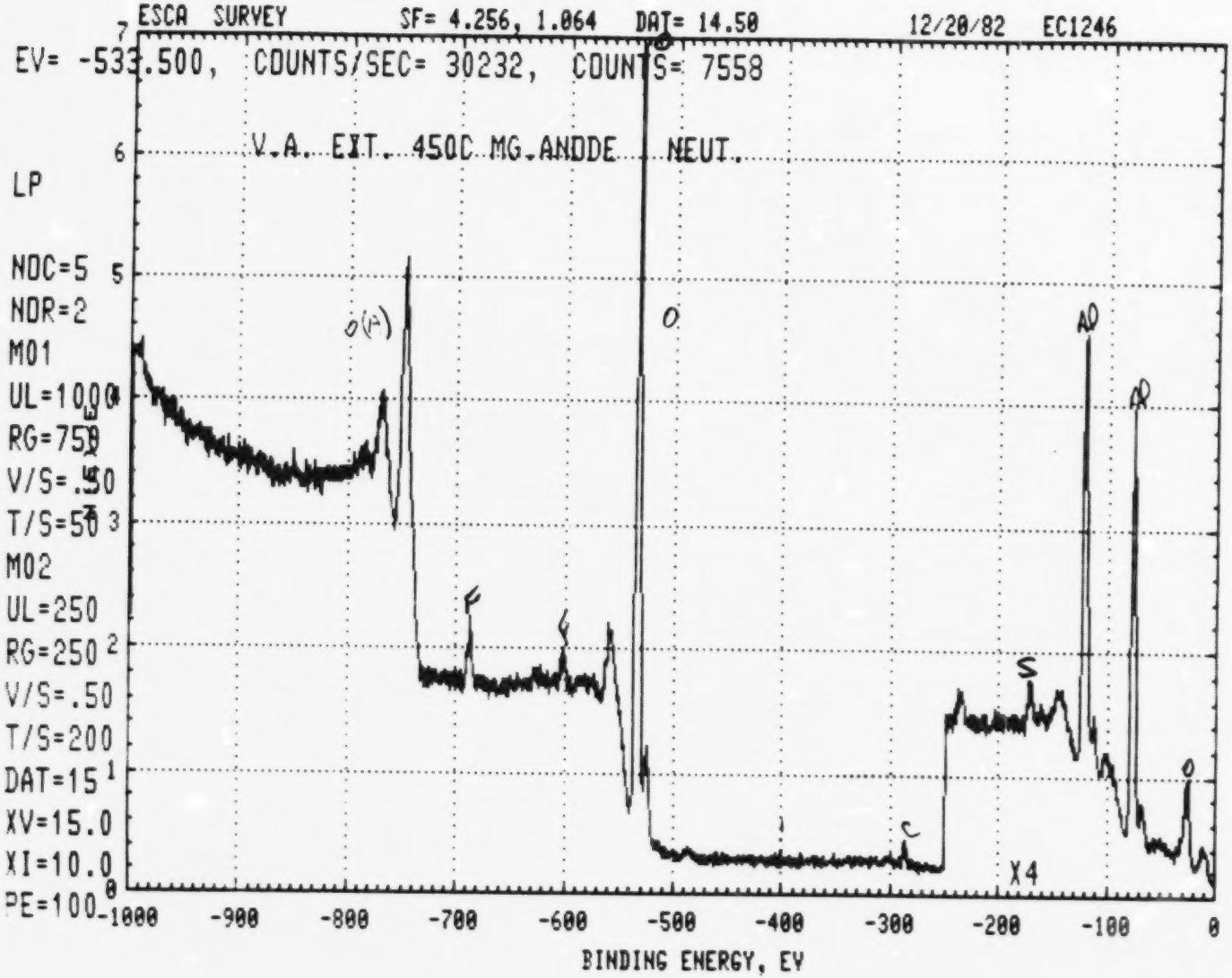
CATALYST MB-VA-FI (CALCINED - 1000°C) AS RECEIVED

Element	XPS		Bulk (Wt.%) (±5%)	Remarks
	At. % (±10%)	Wt. %		
Al	29.4	41.5		- Al_2O_3
O	51.6	43.2		
C	14.5	9.1		- handling in air, vacuum pump oil and muffle furnace contamination.
F	0.6	0.6		- greatly reduced.
Si	3.8	5.6		- muffle furnace contamination. (SiO_2)
				Note: No S or N observed. F/Al = 0.02

TABLE 4

CATALYST MB-VA-FI (CALCINED - 1000°C) FINELY GROUND

Element	XPS		Bulk (Wt.%) (±5%)	Remarks
	At. % (±10%)	Wt. %		
Al	35.2	48.4		- Al_2O_3
O	55.0	44.8		
C	9.0	5.5		- reduced after grinding.
F	0.8	0.8		- slight increase.
Ti	∠0.2	∠0.5		?
				Note: No N,S, or Si - observed. F/Al = 0.023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NOR=2
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UL=1000
RG=750
V/S=.50
T/S=50
M02
UL=250
RG=250
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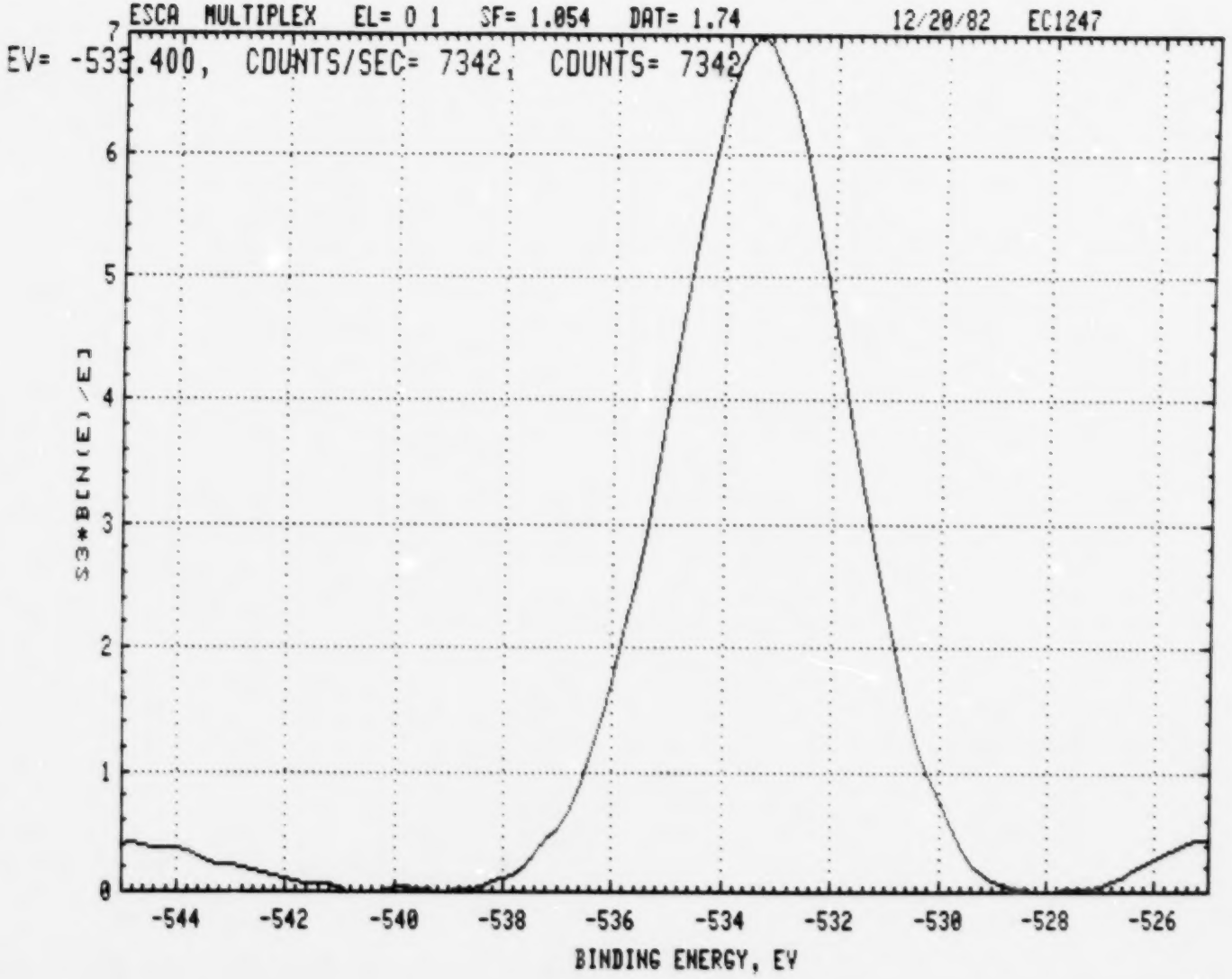
X4
BINDING ENERGY, EV

Figure 1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2
3
4
5
6
7
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-542
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-528
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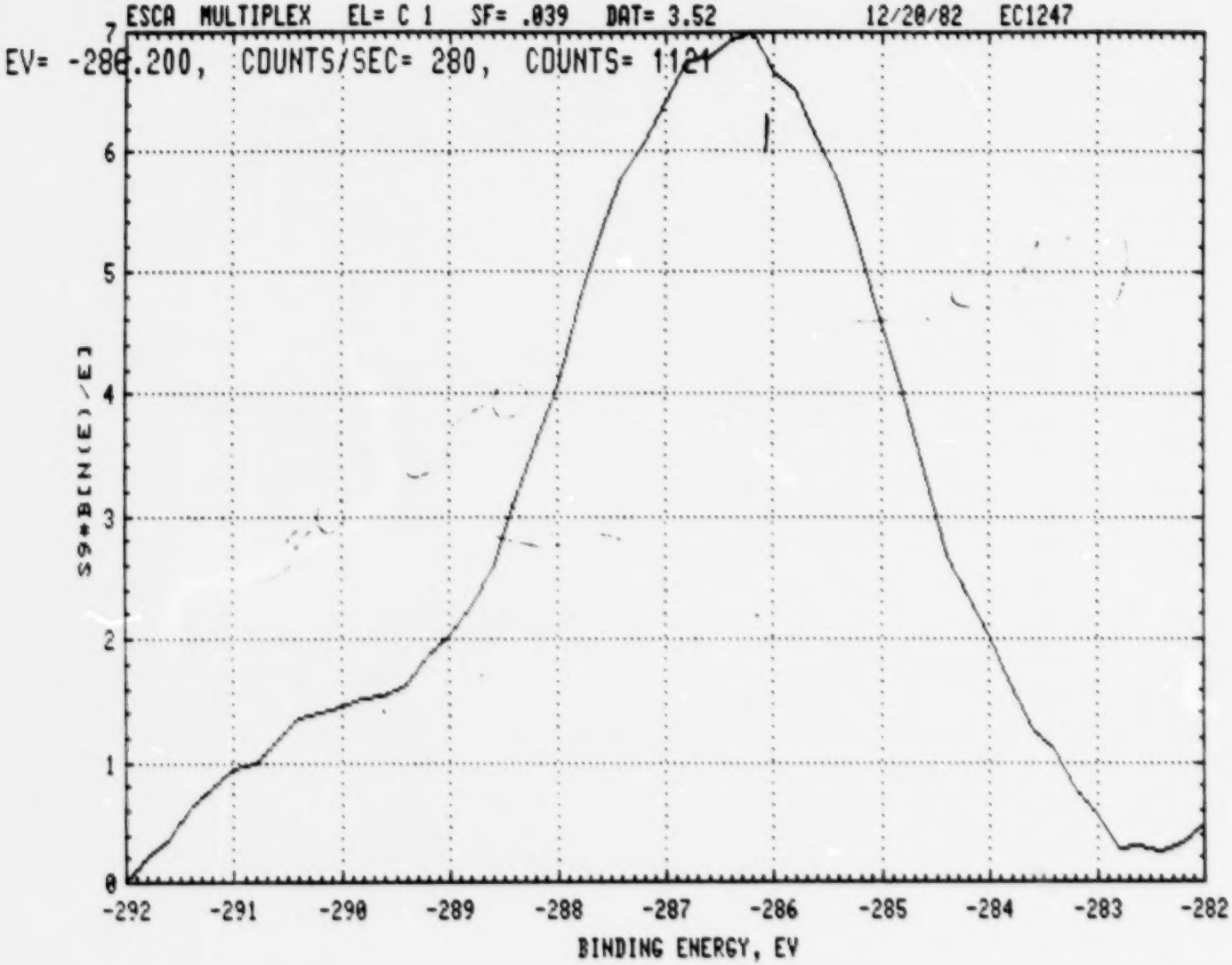
BINDING ENERGY, EV

Figure 2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2
3
4
5
6
7
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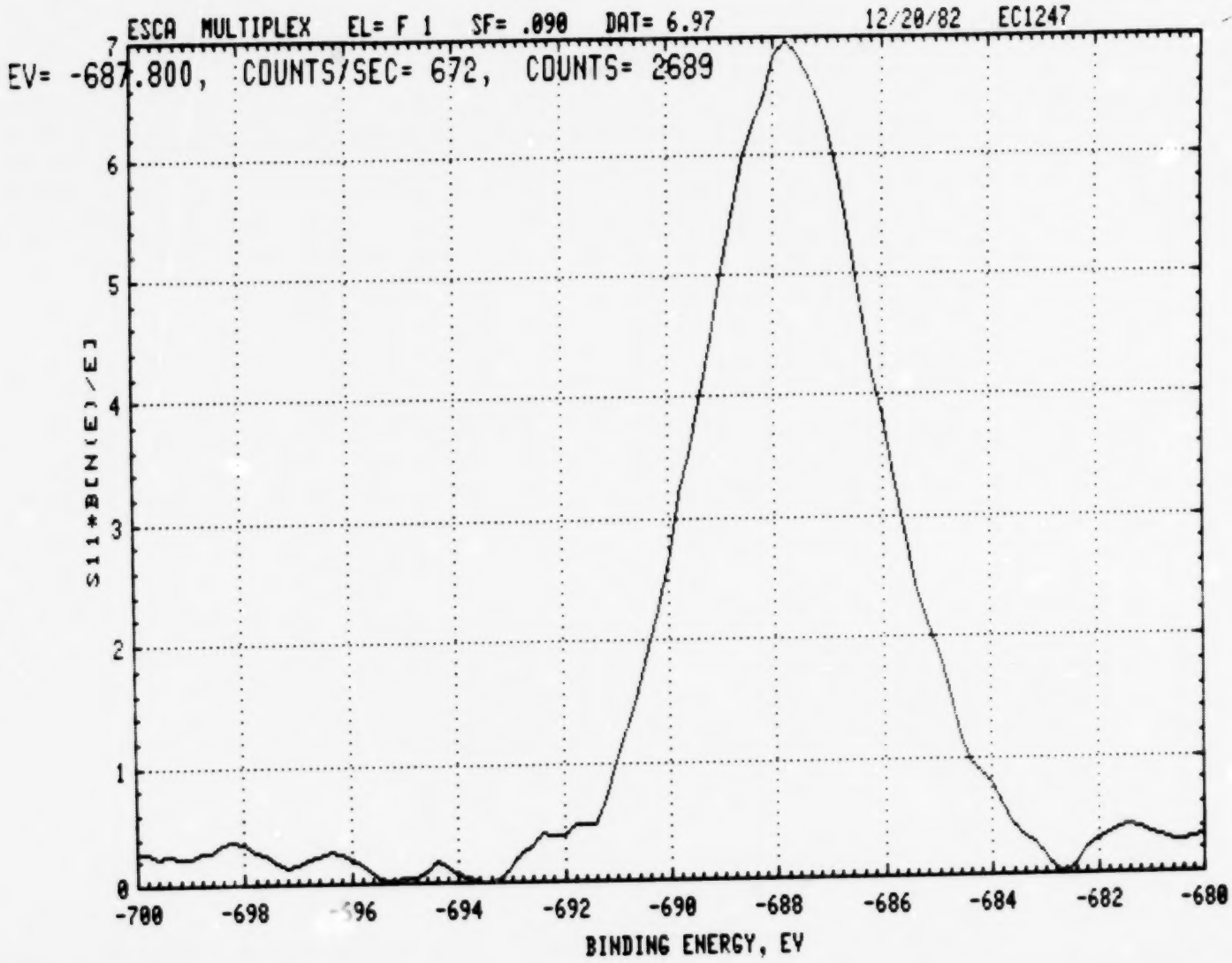
BINDING ENERGY, EV

Figure 3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2
3
4
5
6
7
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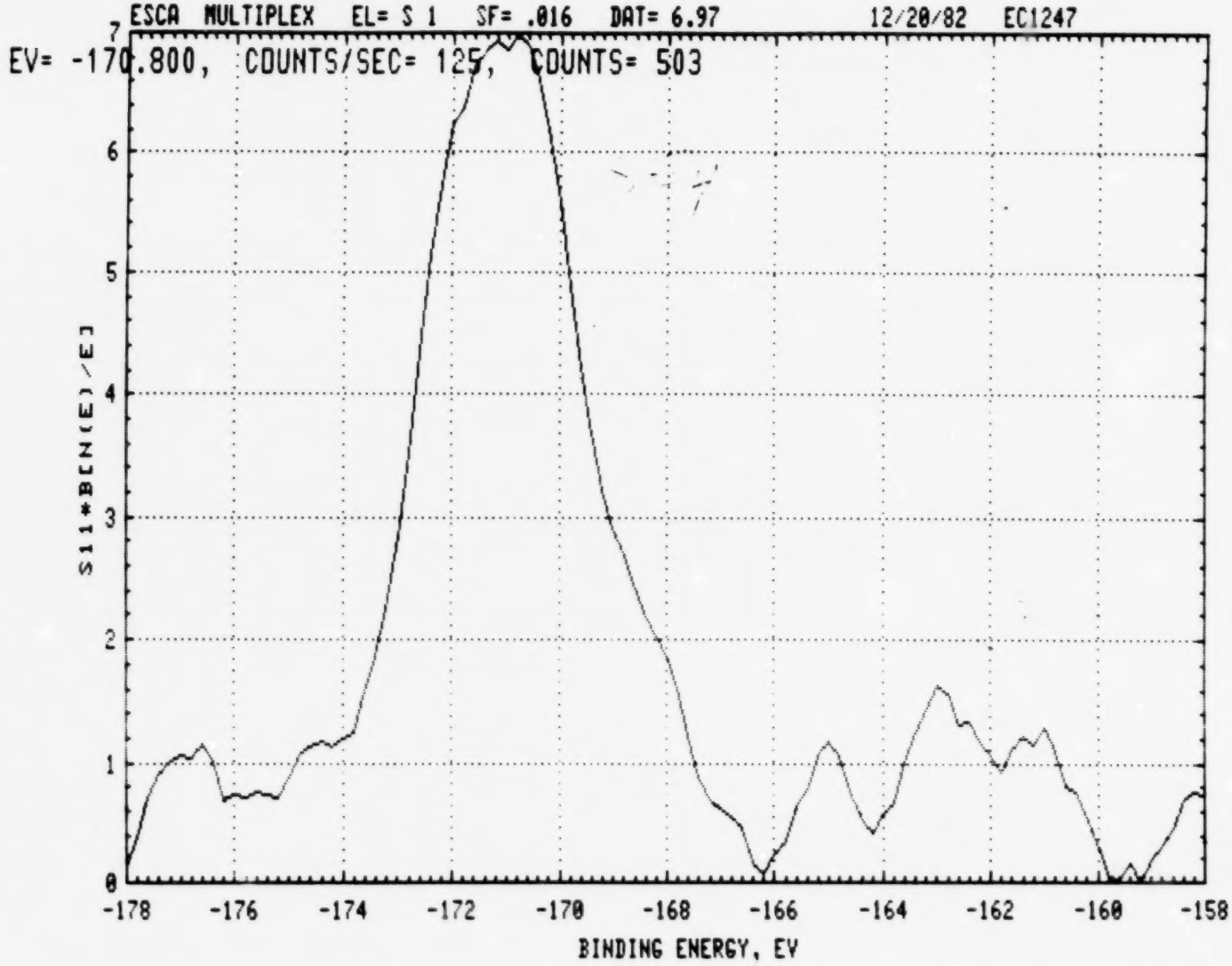
BINDING ENERGY, EV

Figure 4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1
2
3
4
5
6
7
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-176
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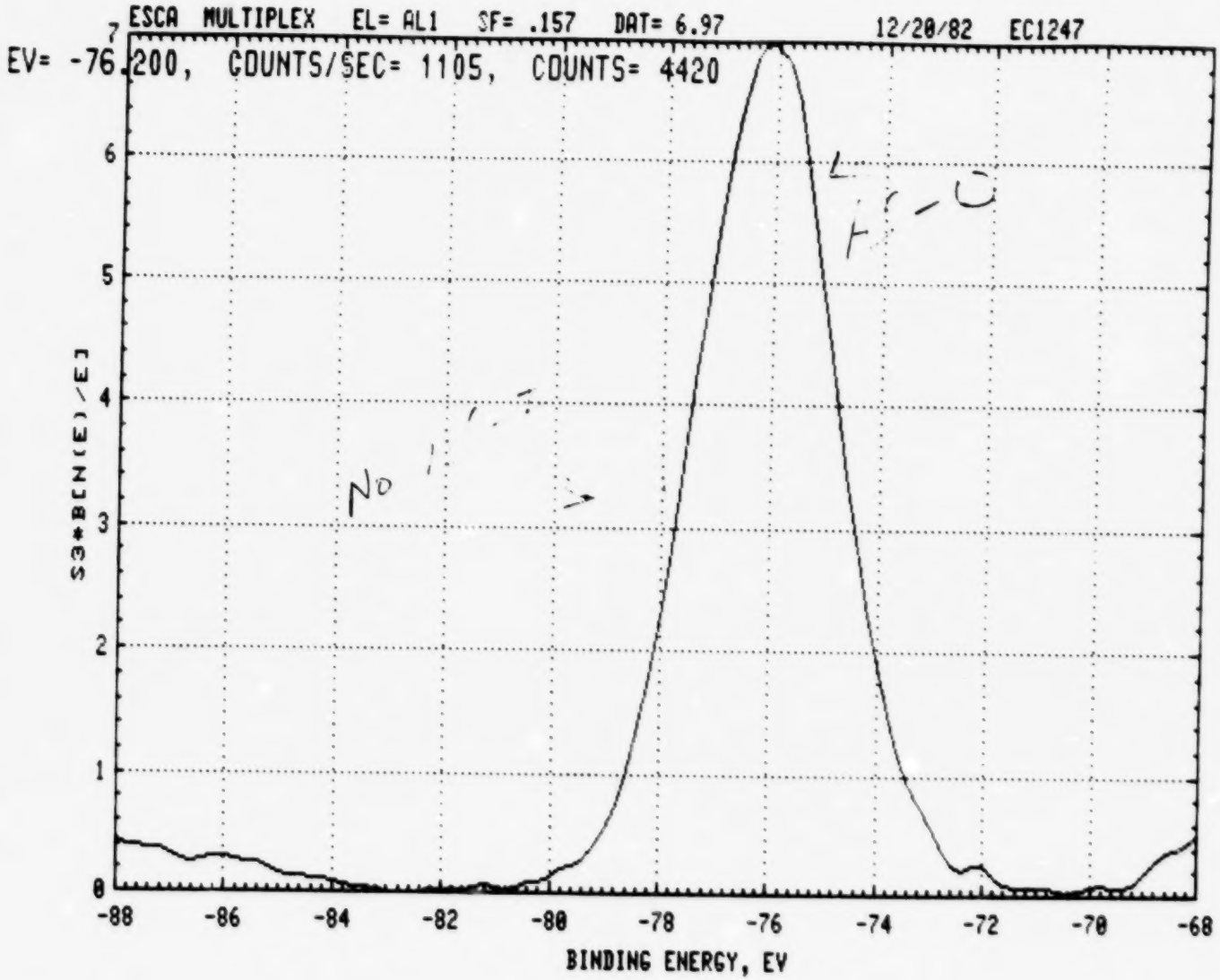
-162
-160
-158
BINDING ENERGY, EV

Figure 5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BINDING ENERGY, EV
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-86
-84
-82
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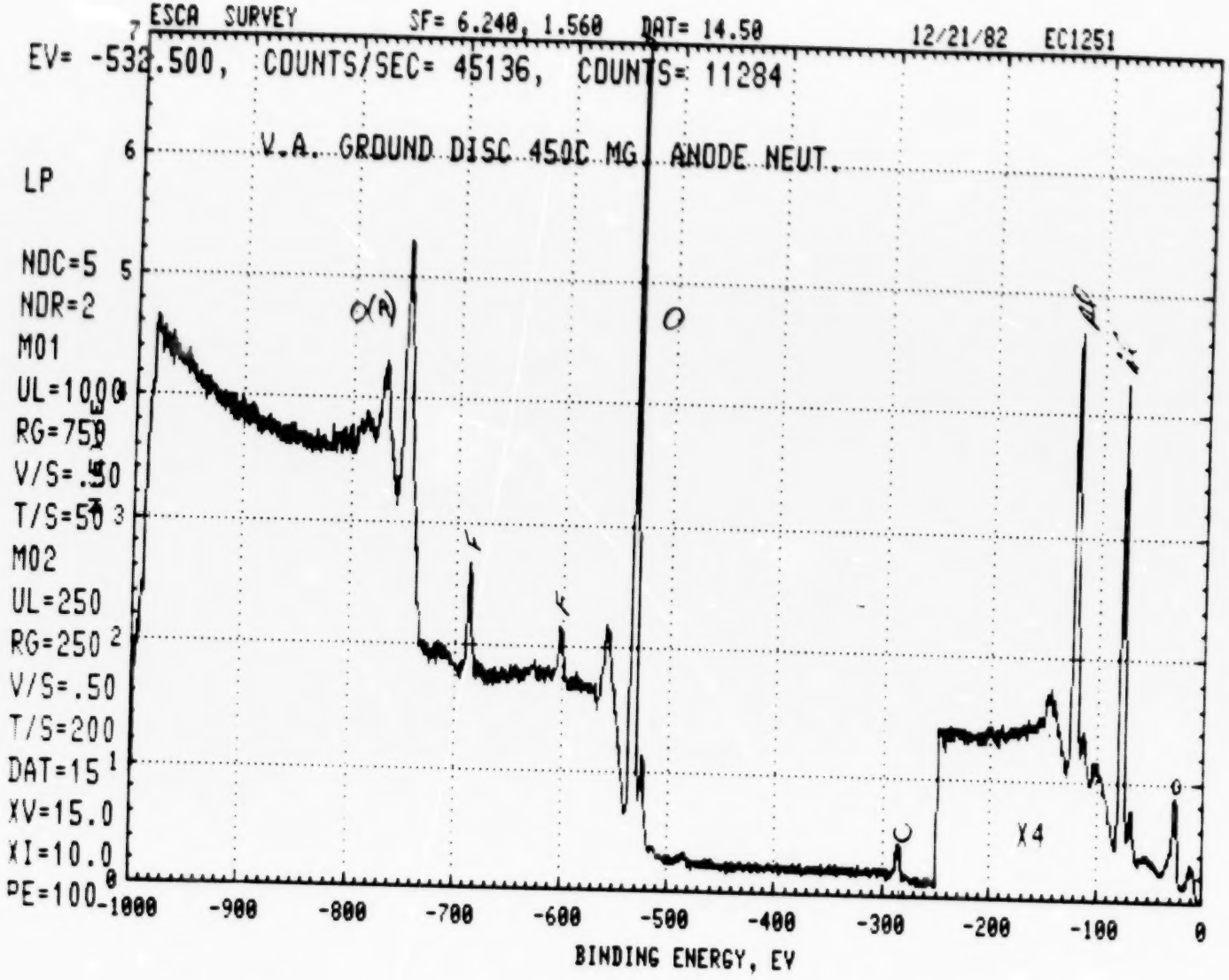
1
2
3
4
5
6
7

Figure 6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M02
UL=250
RG=250
V/S=.50
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DAT=15
XV=15.0
XI=10.0
PE=100
O(A)
O
X4
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-200
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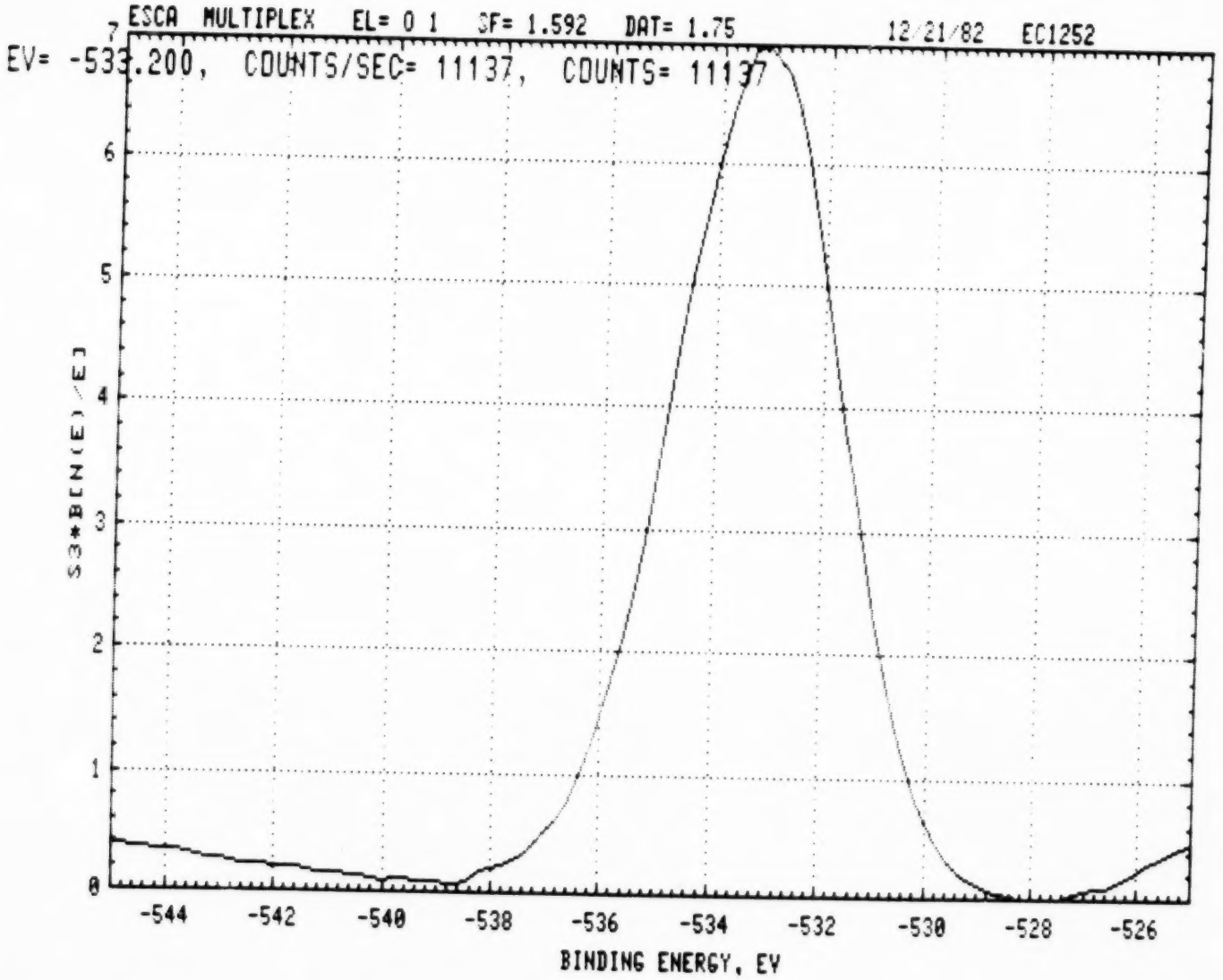
BINDING ENERGY, EV

Figure 7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6
5
4
3
2
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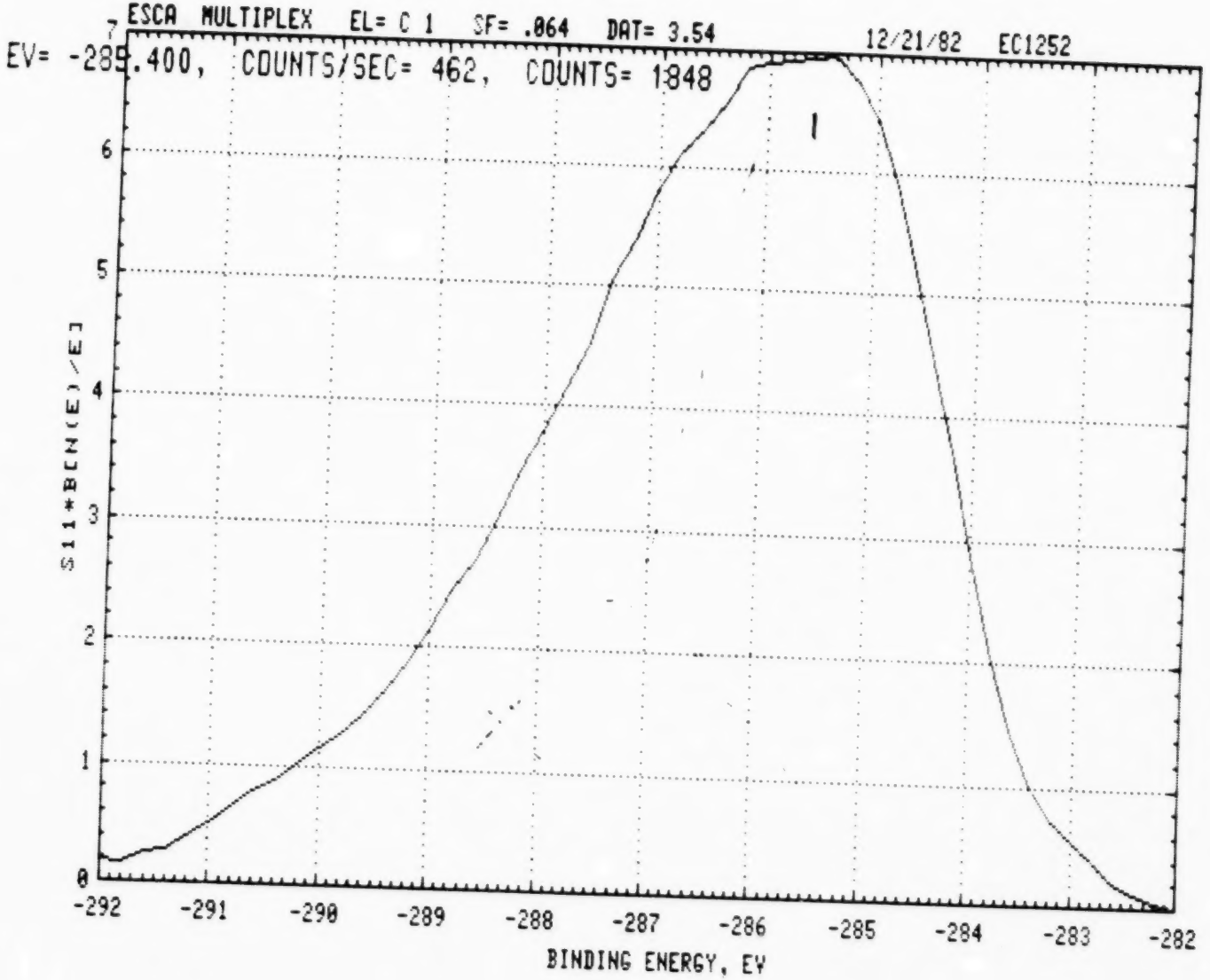
-528
-526
BINDING ENERGY, EV

Figure 8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1
2
3
4
5
6
7
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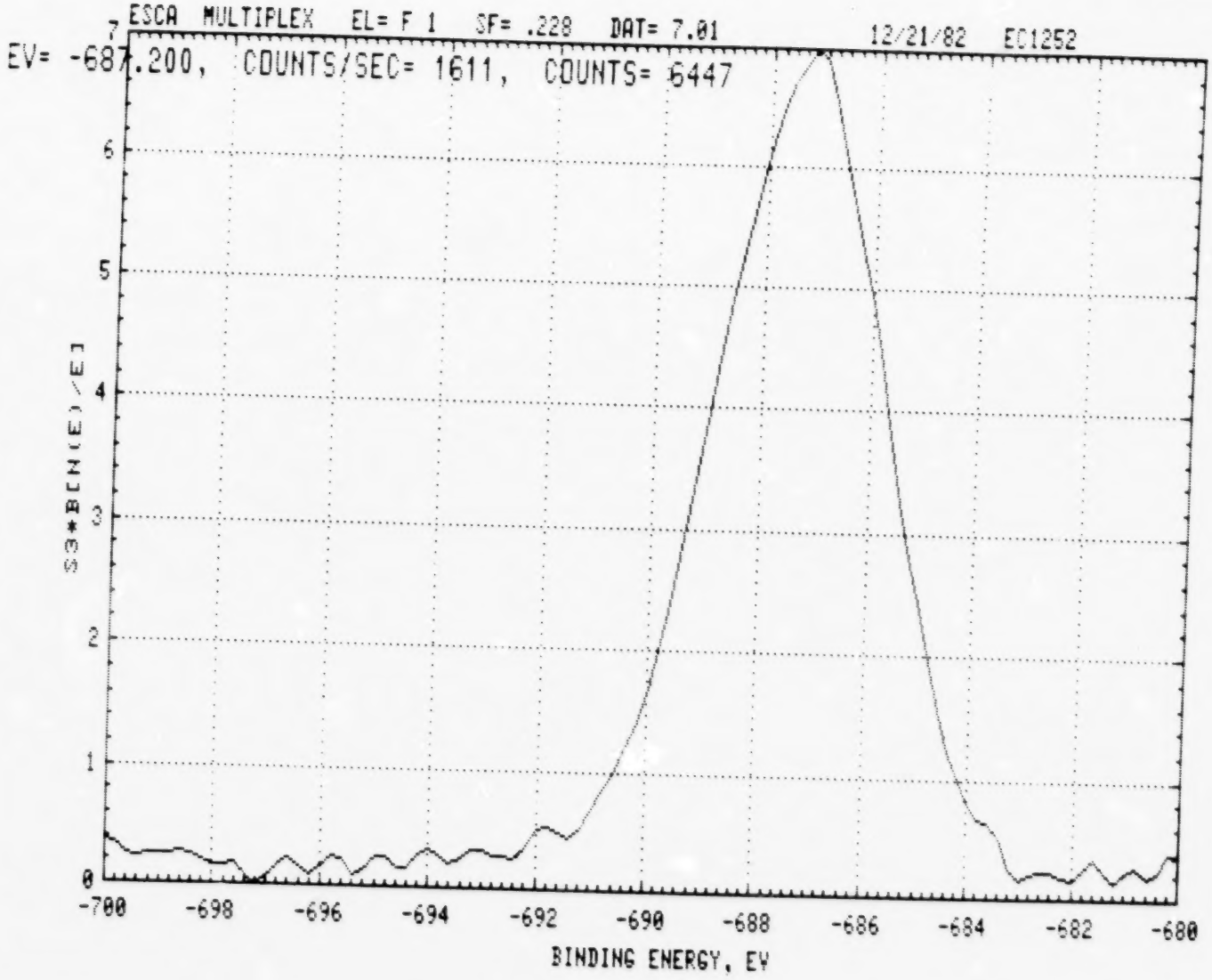
-282
BINDING ENERGY, EV

Figure 9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2
3
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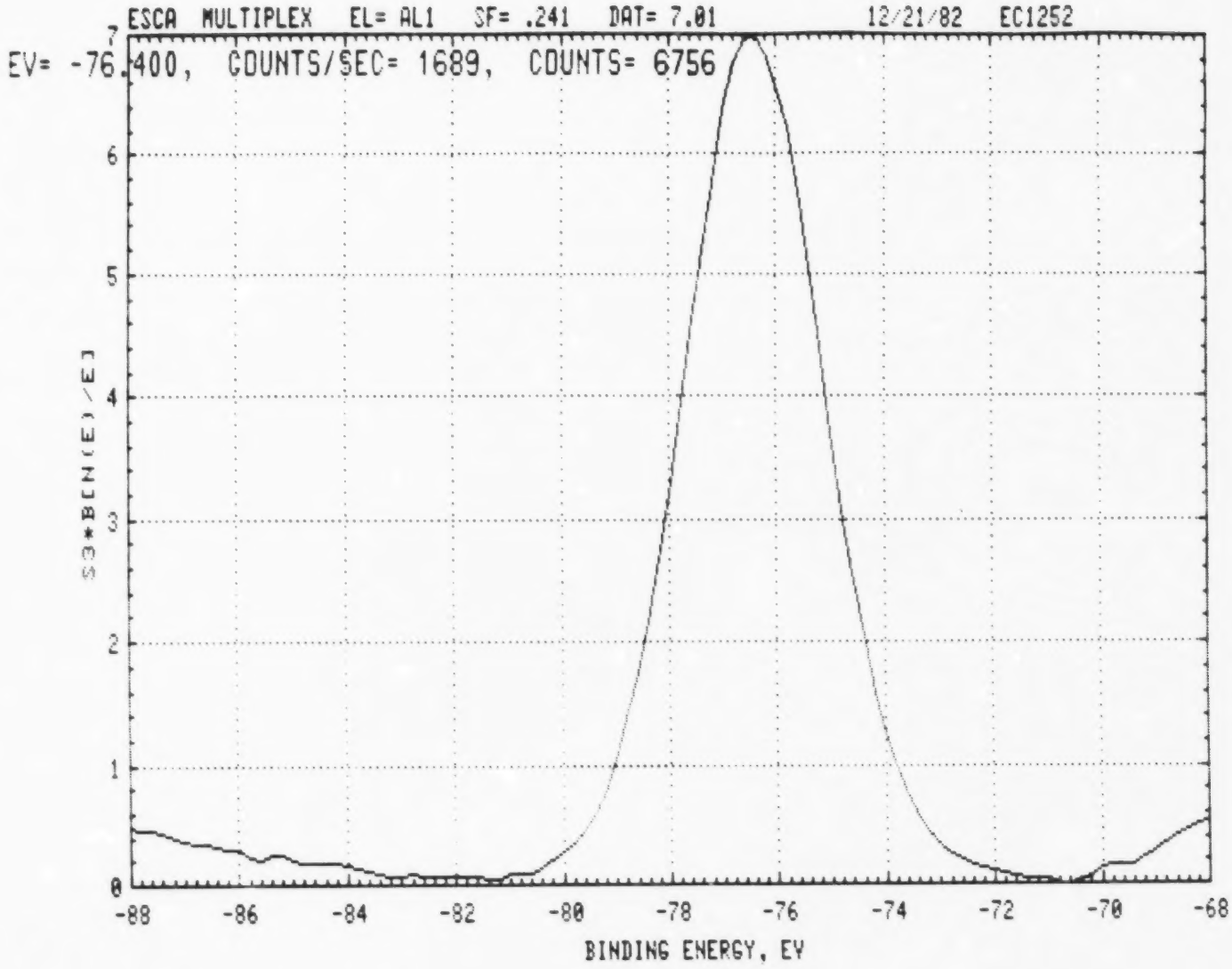
BINDING ENERGY, EV

Figure 10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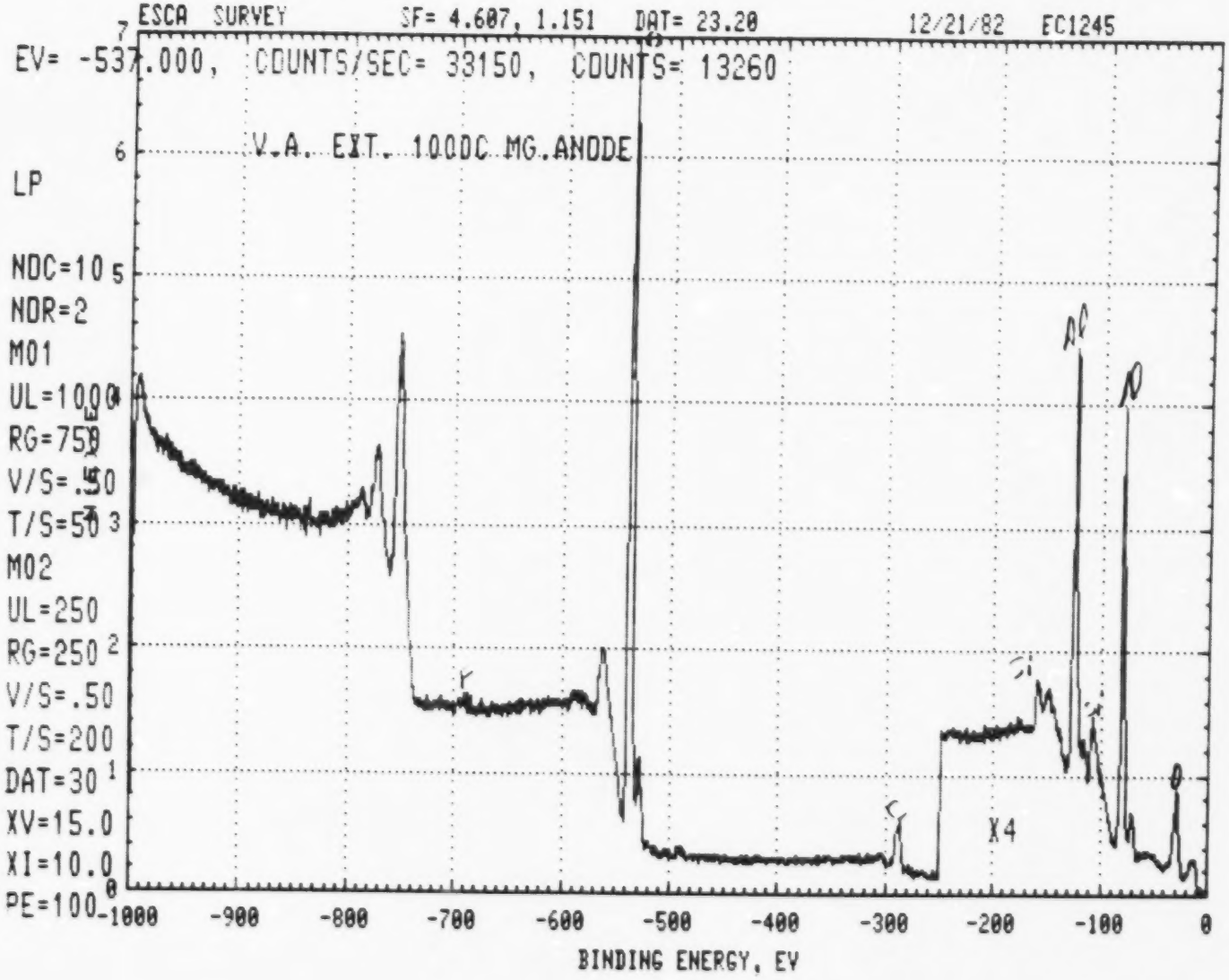
BINDING ENERGY, EV

Figure 11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PE=100
X4
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BINDING ENERGY, EV

Figure 12

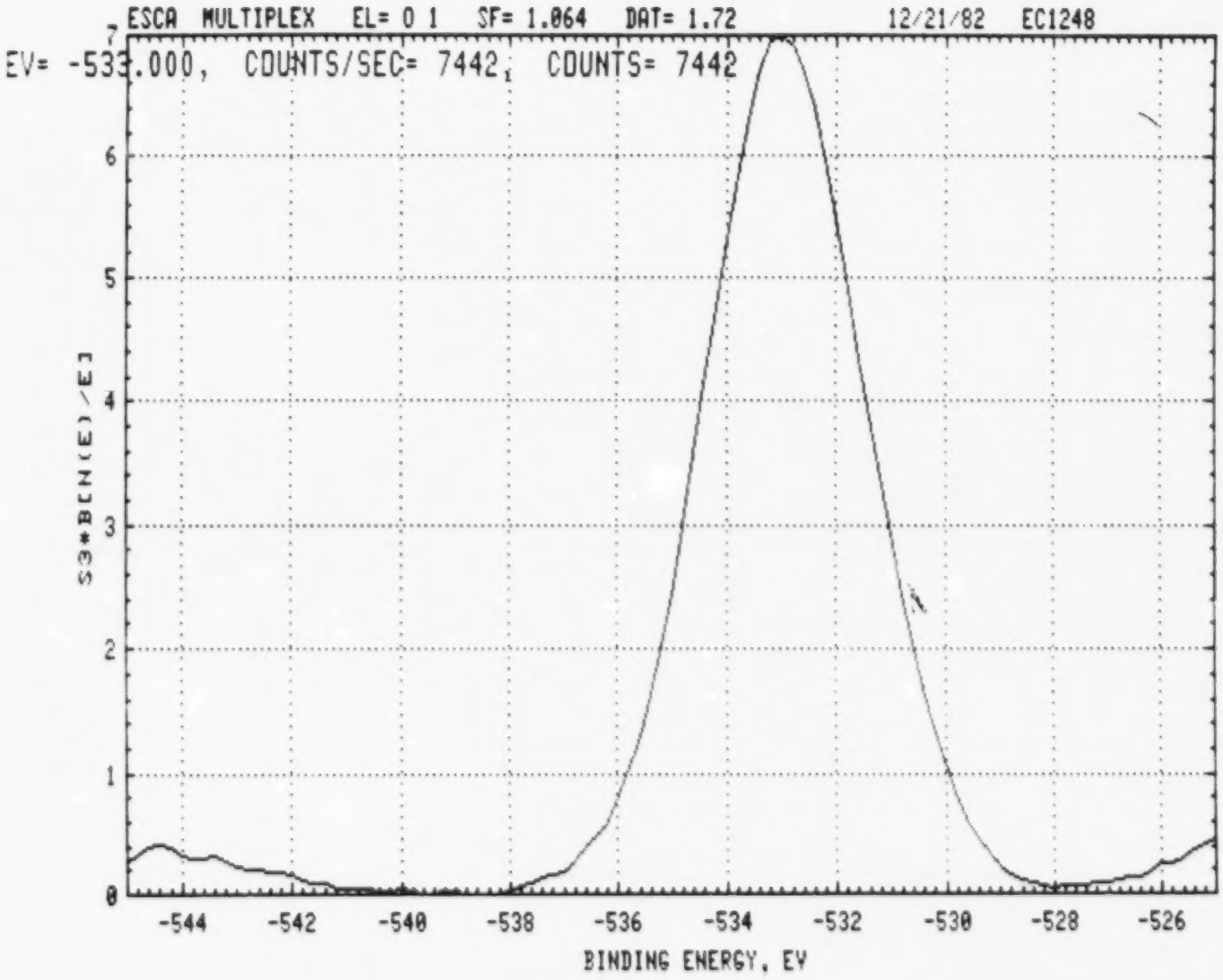
ESCA MULTIPLEX EL= 0 1 SF= 1.064 DAT= 1.72 12/21/82 EC1248
EV= -533.000, COUNTS/SEC= 7442, COUNTS= 7442
S3*BCN(E)/E
7
6
5
4
3
2
1
0
-544
-542
-540
-538
-536
-534
-532
-530
-528
-526
BINDING ENERGY, EV

Figure 13

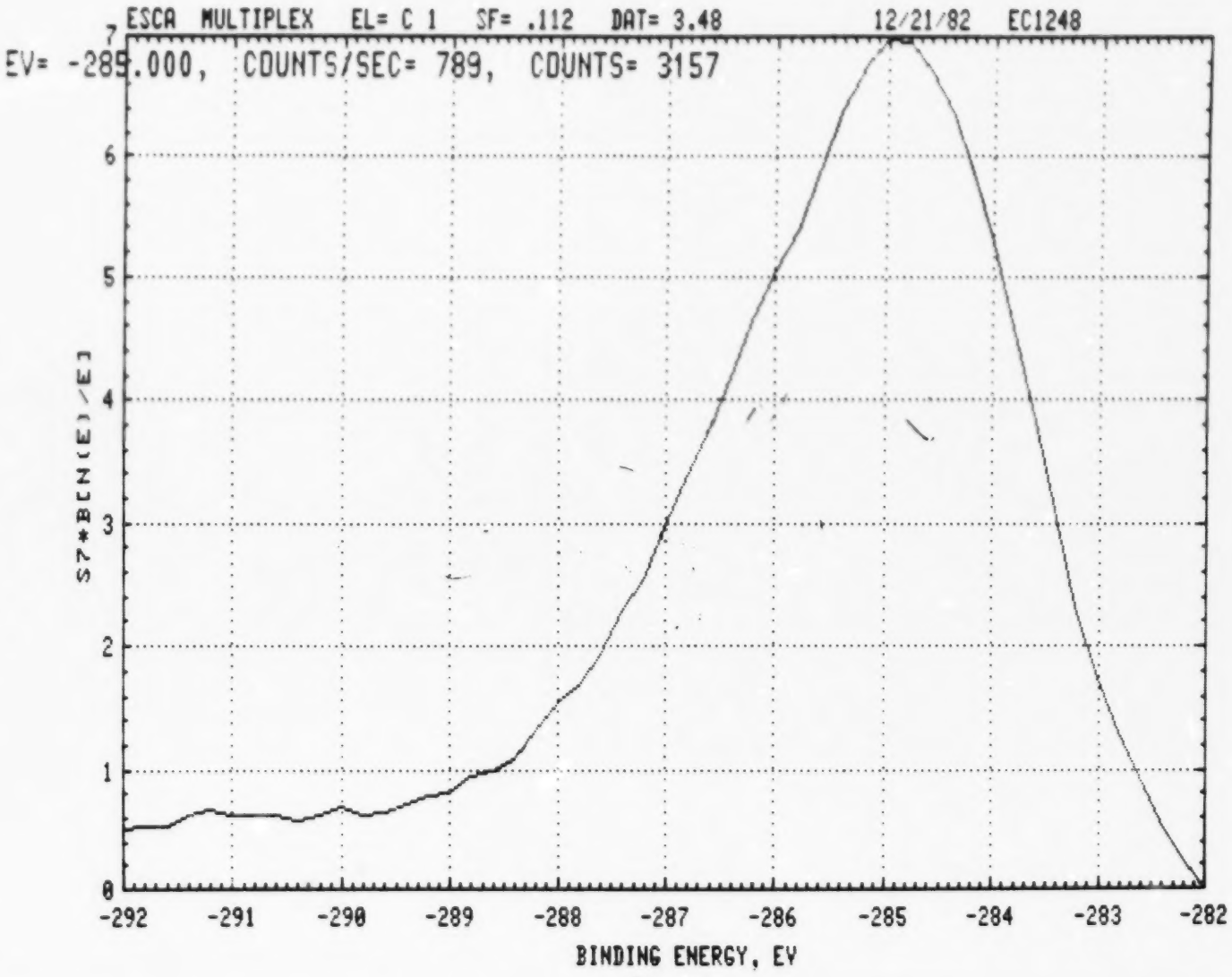
ESCA MULTIPLEX EL= C 1 SF= .112 DAT= 3.48 12/21/82 EC1248
EV= -285.000, COUNTS/SEC= 789, COUNTS= 3157
S7*BCN(E)/E]
0
1
2
3
4
5
6
7
-292
-291
-290
-289
-288
-287
-286
-285
-284
-283
-282
BINDING ENERGY, EV

Figure 14

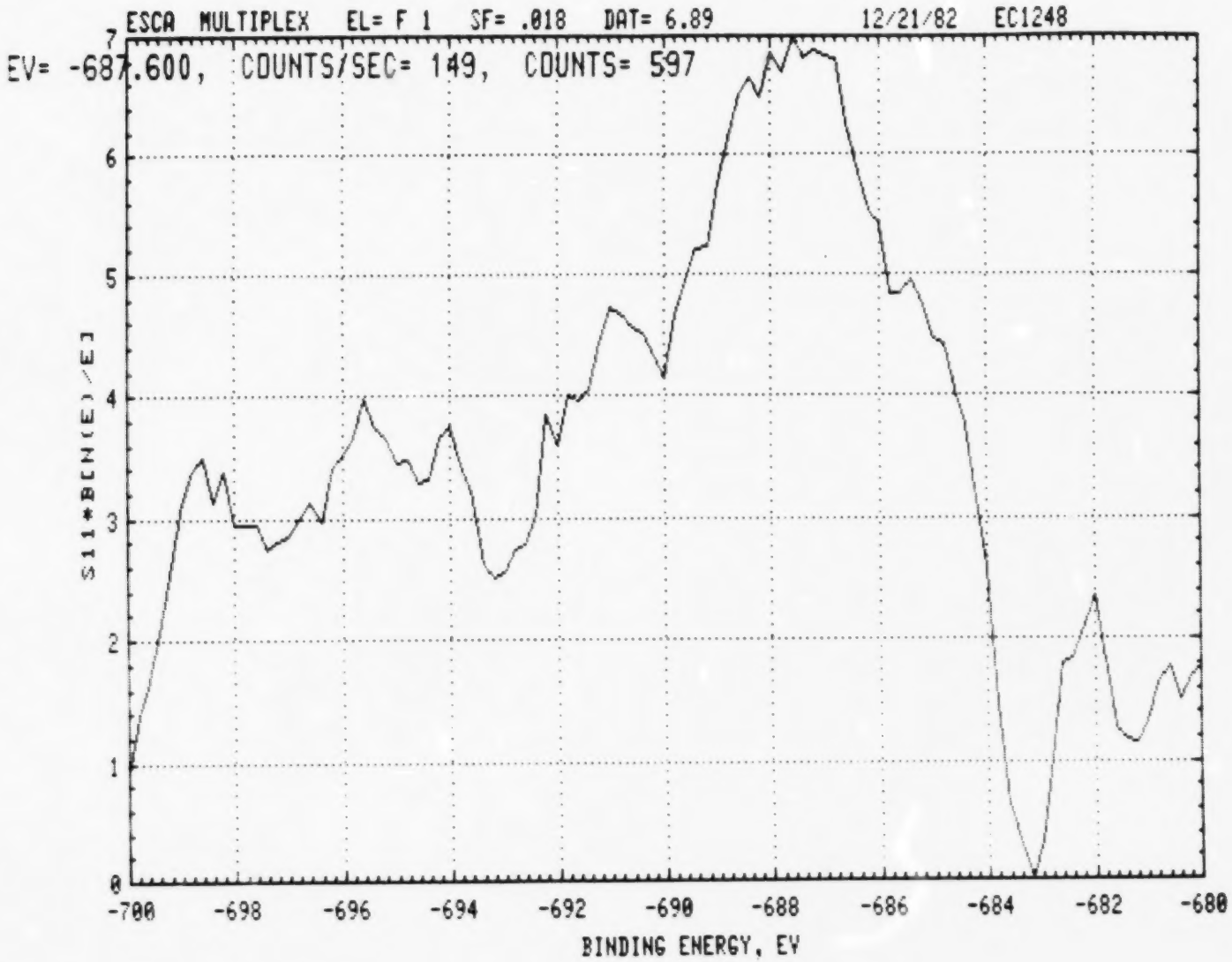
ESCA MULTIPLEX EL= F 1 SF= .018 DAT= 6.89 12/21/82 EC1248
EV= -687.600, COUNTS/SEC= 149, COUNTS= 597
S11*BCN(E)/E]
0
1
2
3
4
5
6
7
-700
-698
-696
-694
-692
-690
-688
-686
-684
-682
-680
BINDING ENERGY, EV

Figure 15

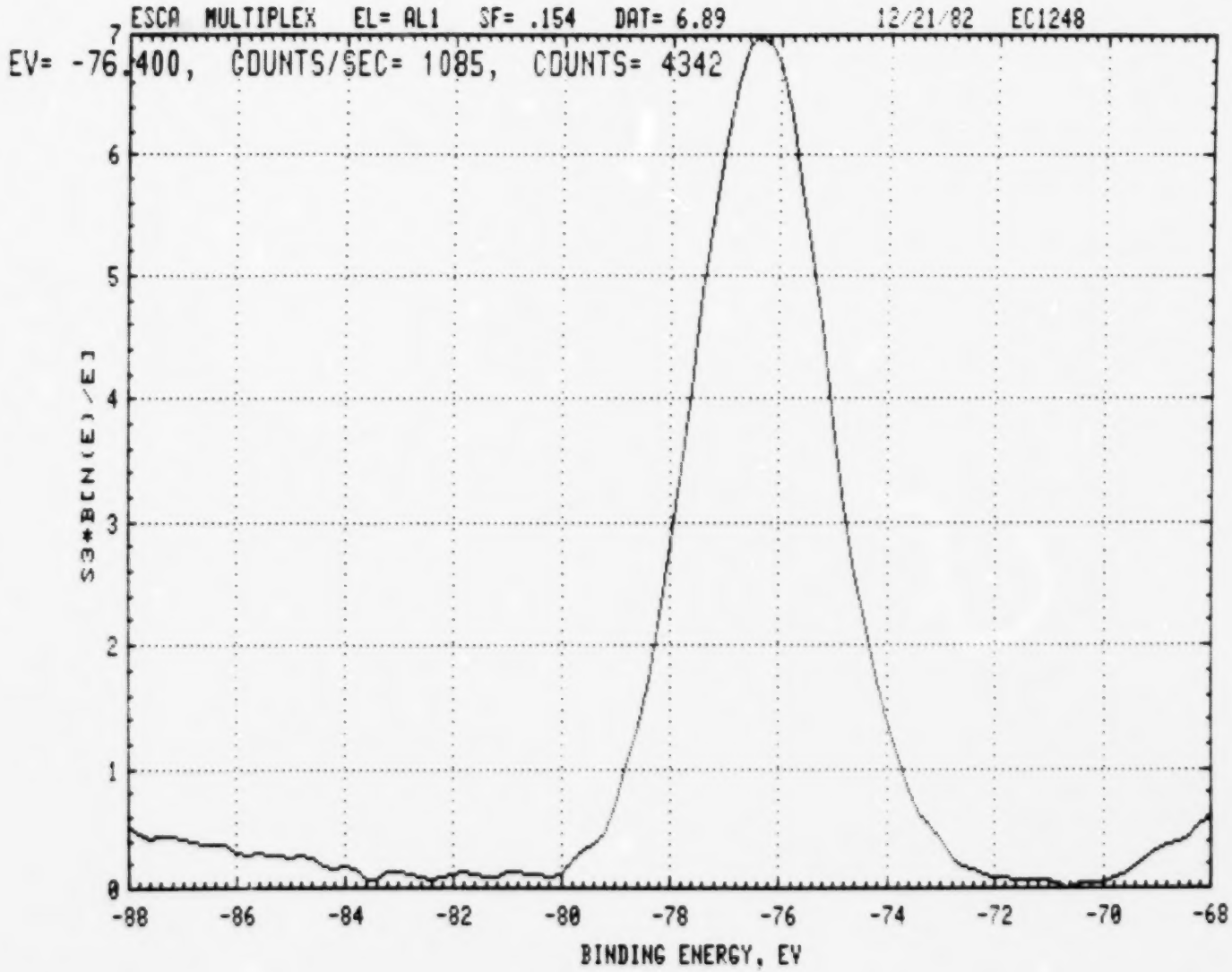
ESCA MULTIPLEX EL= AL1 SF= .154 DAT= 6.89 12/21/82 EC1248
EV= -76.400, COUNTS/SEC= 1085, COUNTS= 4342
S3*BCN(E)/E]
BINDING ENERGY, EV
0
1
2
3
4
5
6
7
-88
-86
-84
-82
-80
-78
-76
-74
-72
-70
-68

Figure 16

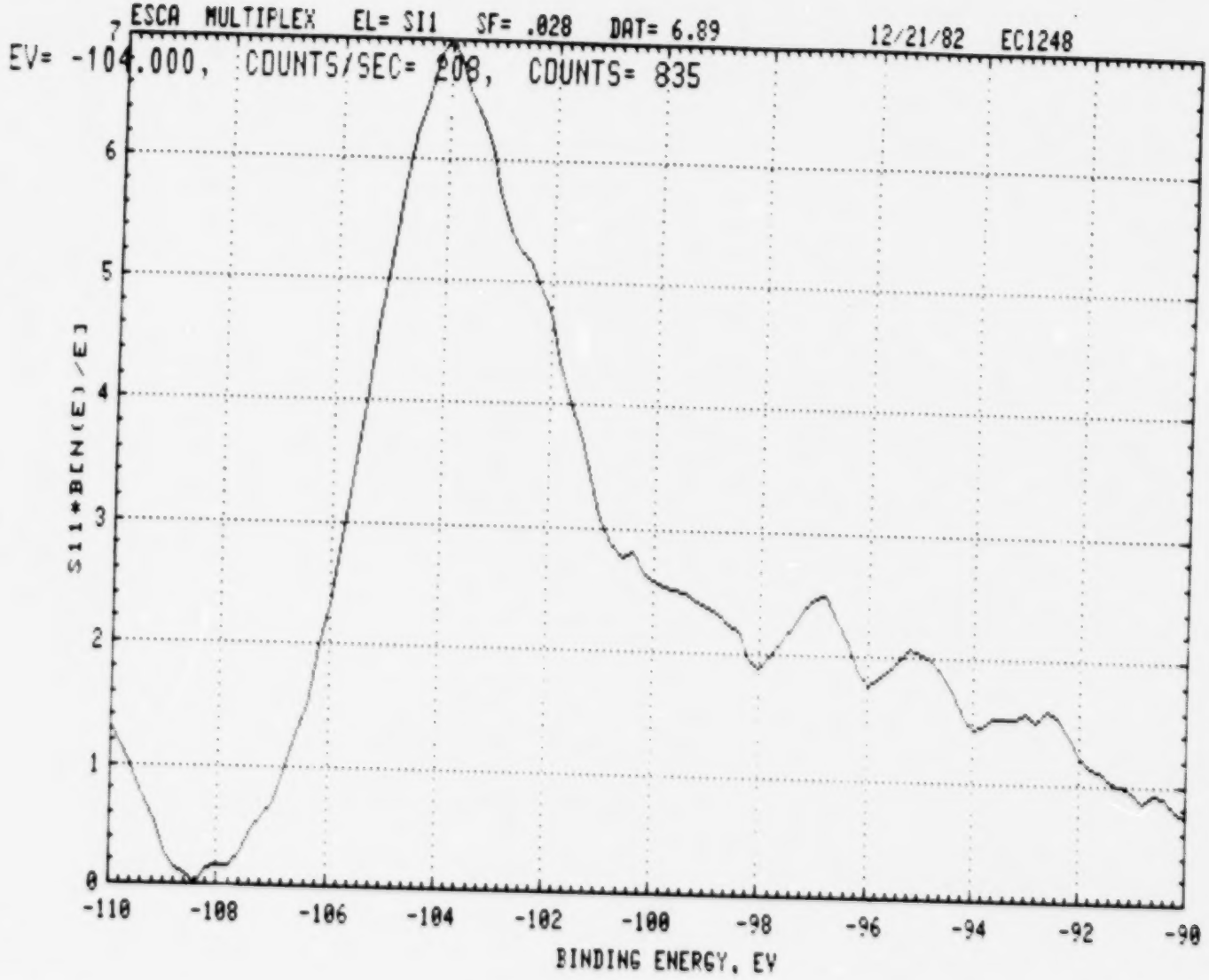
ESCA MULTIPLEX EL= SI1 SF= .028 DAT= 6.89 12/21/82 EC1248
EV= -104.000, COUNTS/SEC= 208, COUNTS= 835
SI1*BEN(E)/E]
BINDING ENERGY, EV
-110
-108
-106
-104
-102
-100
-98
-96
-94
-92
-90
0
1
2
3
4
5
6
7

Figure 17

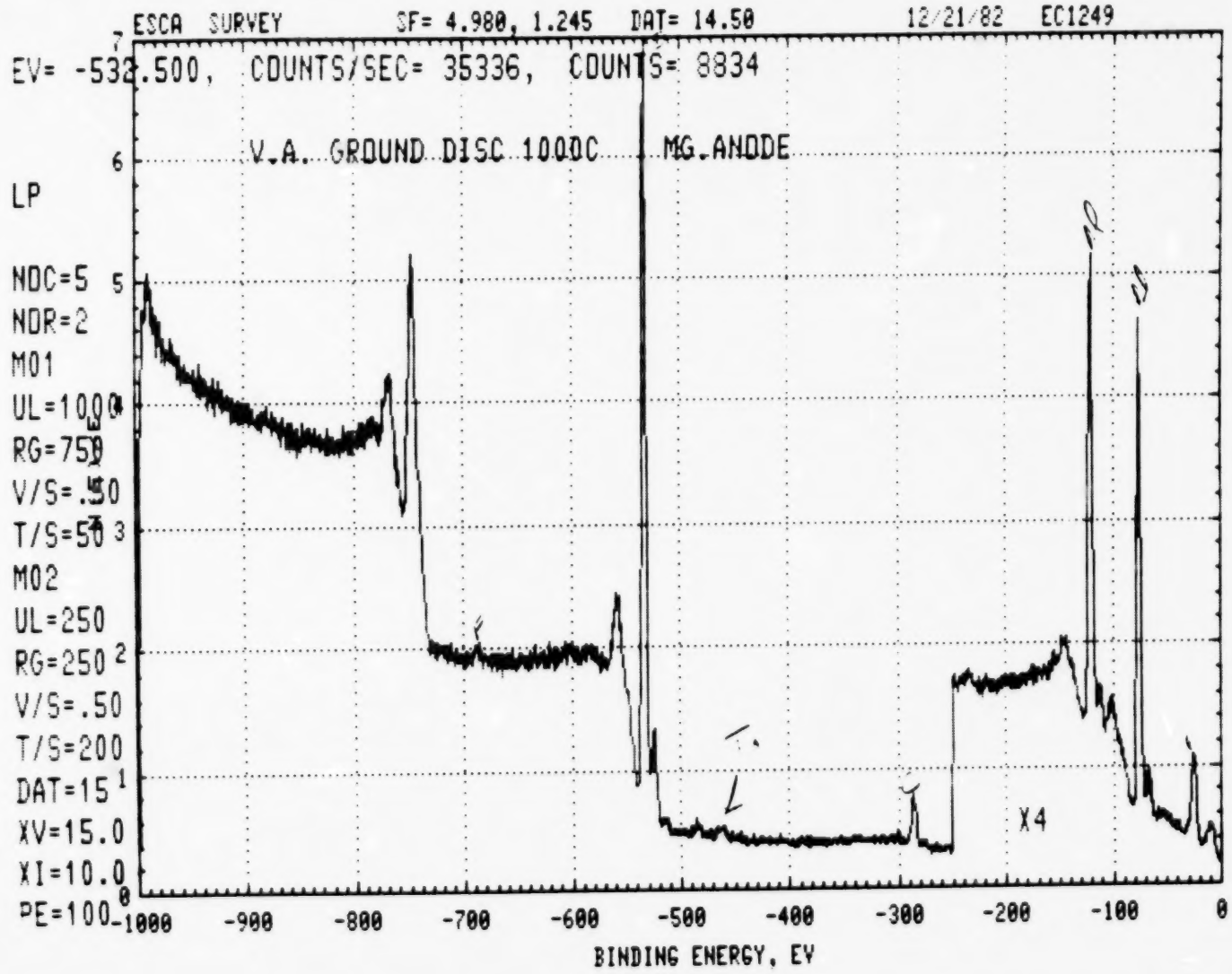
ESCA SURVEY SF= 4.980, 1.245 DAT= 14.50 12/21/82 EC1249
EV= -532.500, COUNTS/SEC= 35336, COUNTS= 8834
V.A. GROUND DISC 1000C MG.ANODE
LP
NOC=5
NOR=2
M01
UL=1000
RG=750
V/S=.50
T/S=50
M02
UL=250
RG=250
V/S=.50
T/S=200
DAT=15
XV=15.0
XI=10.0
PE=100
X4
-1000 -900 -800 -700 -600 -500 -400 -300 -200 -100 0
BINDING ENERGY, EV

Figure 18

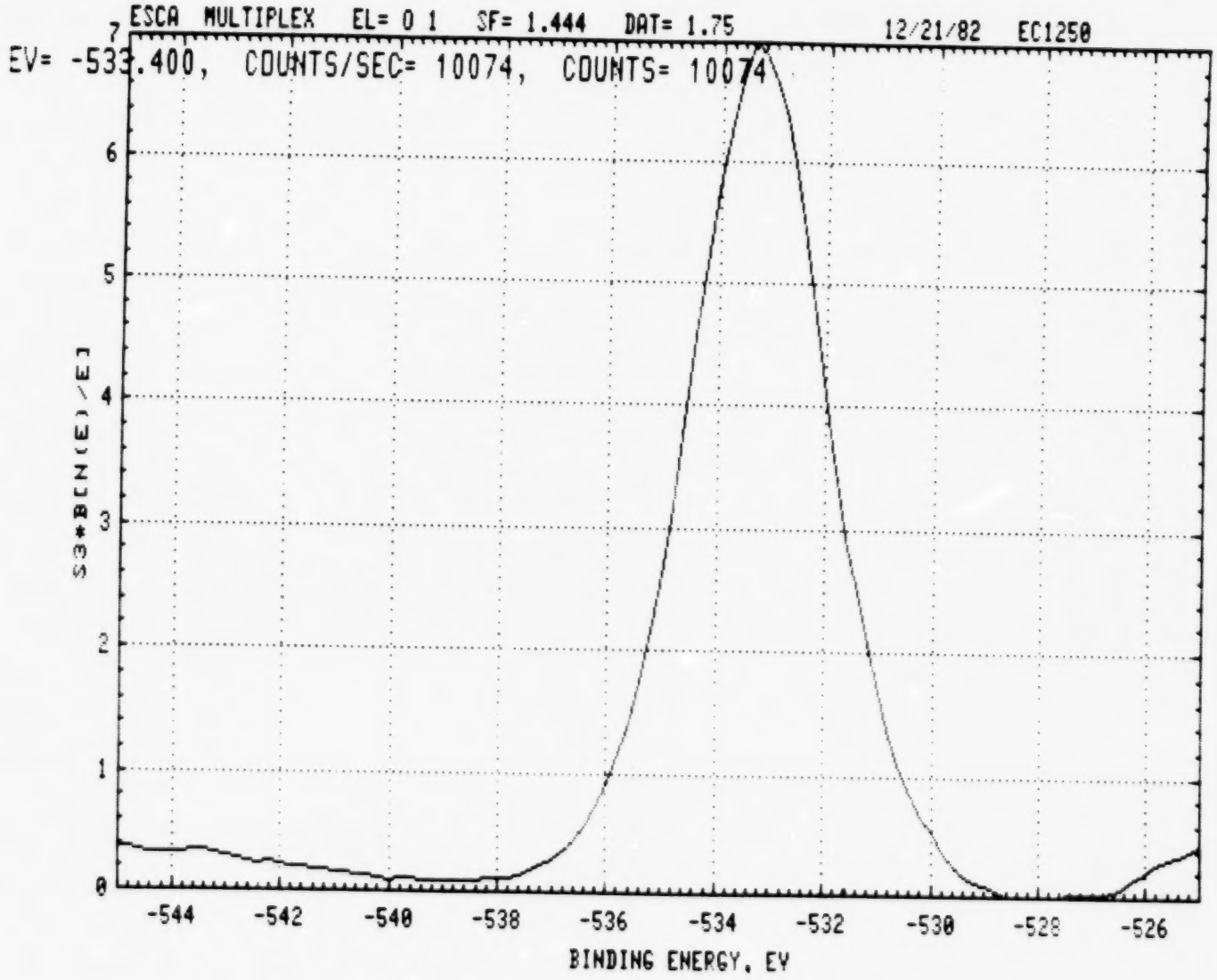
ESCA MULTIPLEX EL= 0 1 SF= 1.444 DAT= 1.75 12/21/82 EC1250
EV= -533.400, COUNTS/SEC= 10074, COUNTS= 10074
S3*BCN(E)/E]
BINDING ENERGY, EV
7
6
5
4
3
2
1
0
-544
-542
-540
-538
-536
-534
-532
-530
-528
-526

Figure 19

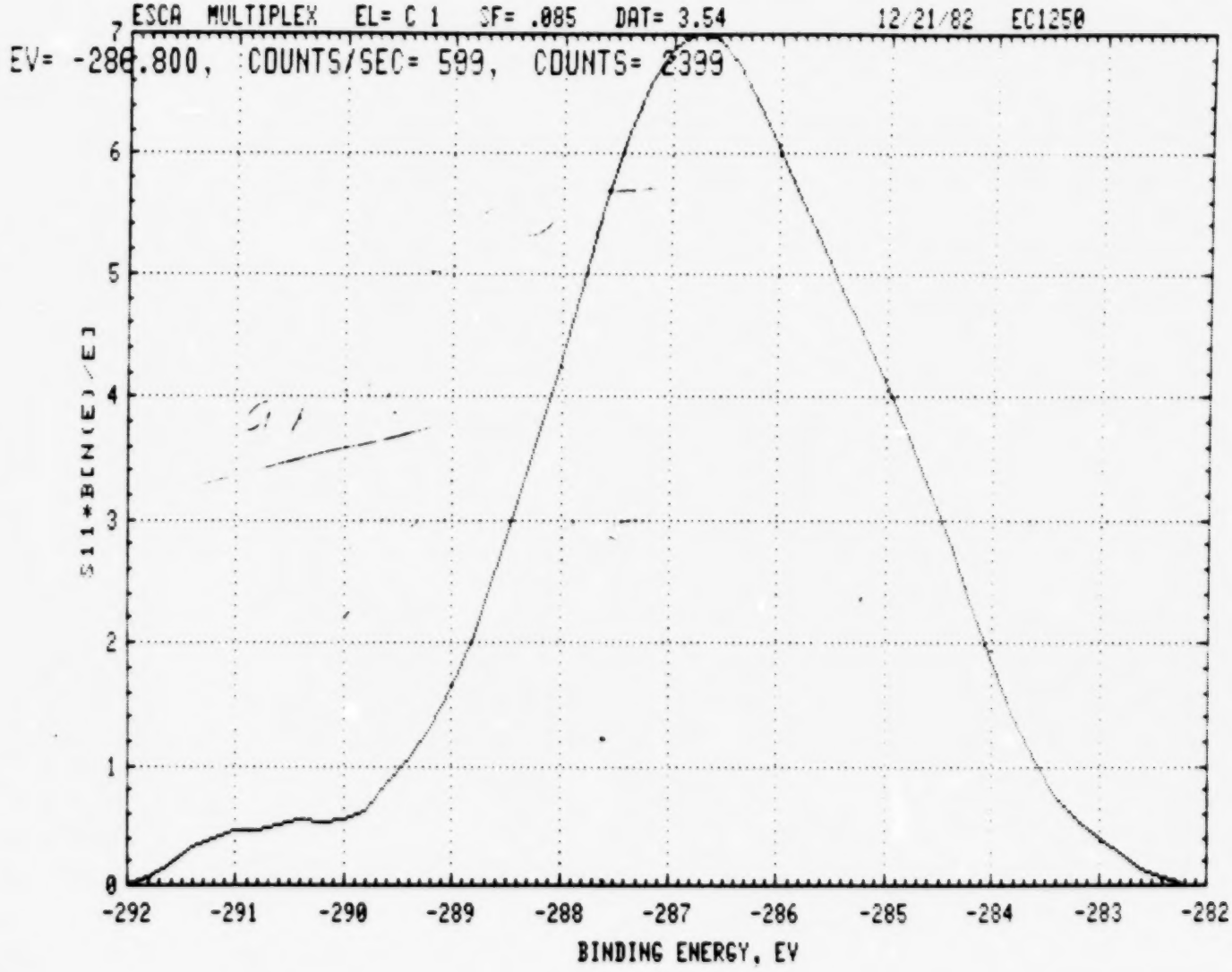
ESCA MULTIPLEX EL= C 1 SF= .085 DAT= 3.54 12/21/82 EC1250
EV= -286.800, COUNTS/SEC= 599, COUNTS= 2399
S11*BCN(E)/E]
7
6
5
4
3
2
1
0
-292
-291
-290
-289
-288
-287
-286
-285
-284
-283
-282
BINDING ENERGY, EV

Figure 20

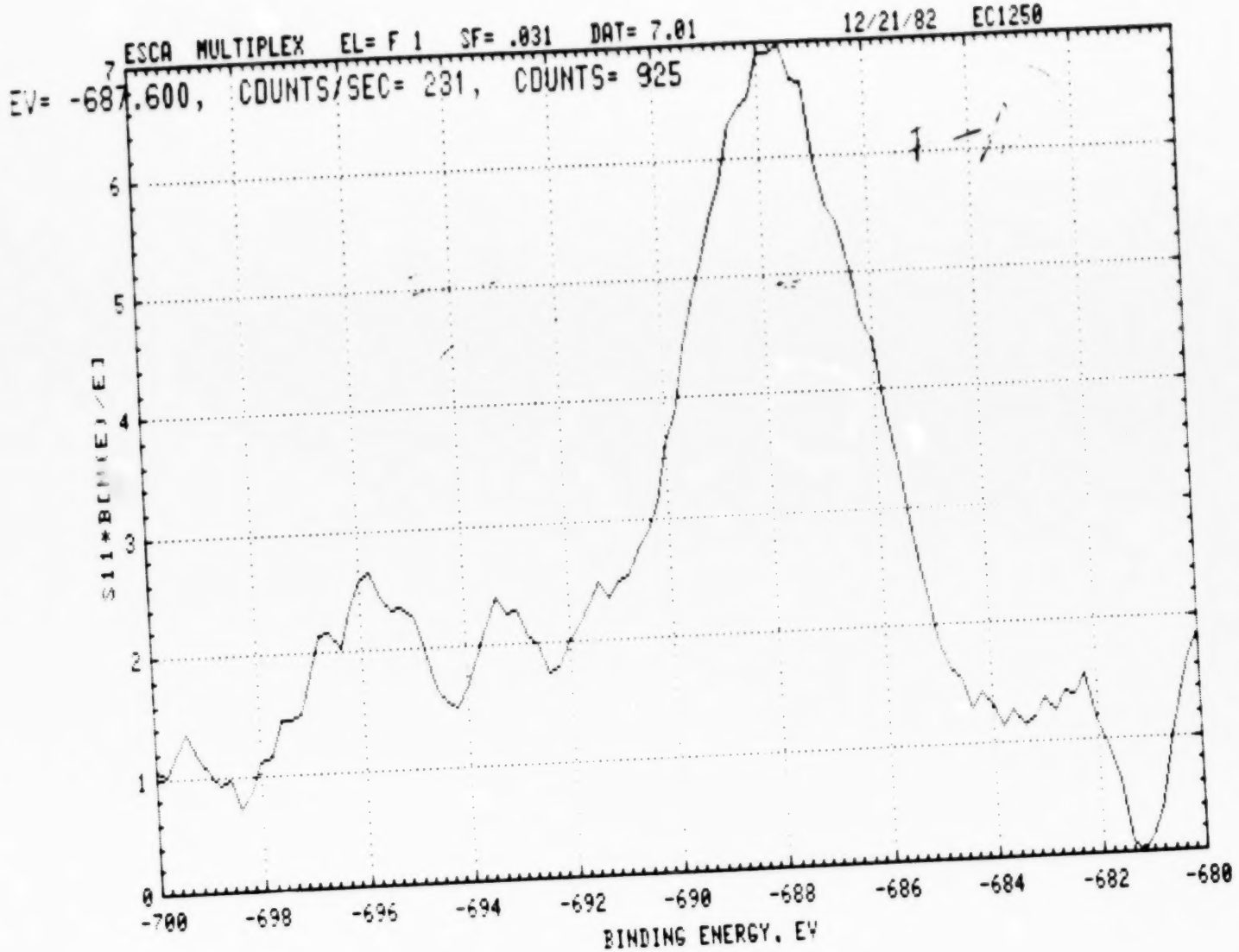
ESCA MULTIPLEX EL= F 1 SF= .031 DAT= 7.01
12/21/82 EC1250
EV= -687.600, COUNTS/SEC= 231, COUNTS= 925
S11*BCKNE)/E]
BINDING ENERGY, EV
0
1
2
3
4
5
6
7
-700
-698
-696
-694
-692
-690
-688
-686
-684
-682
-680

Figure 21

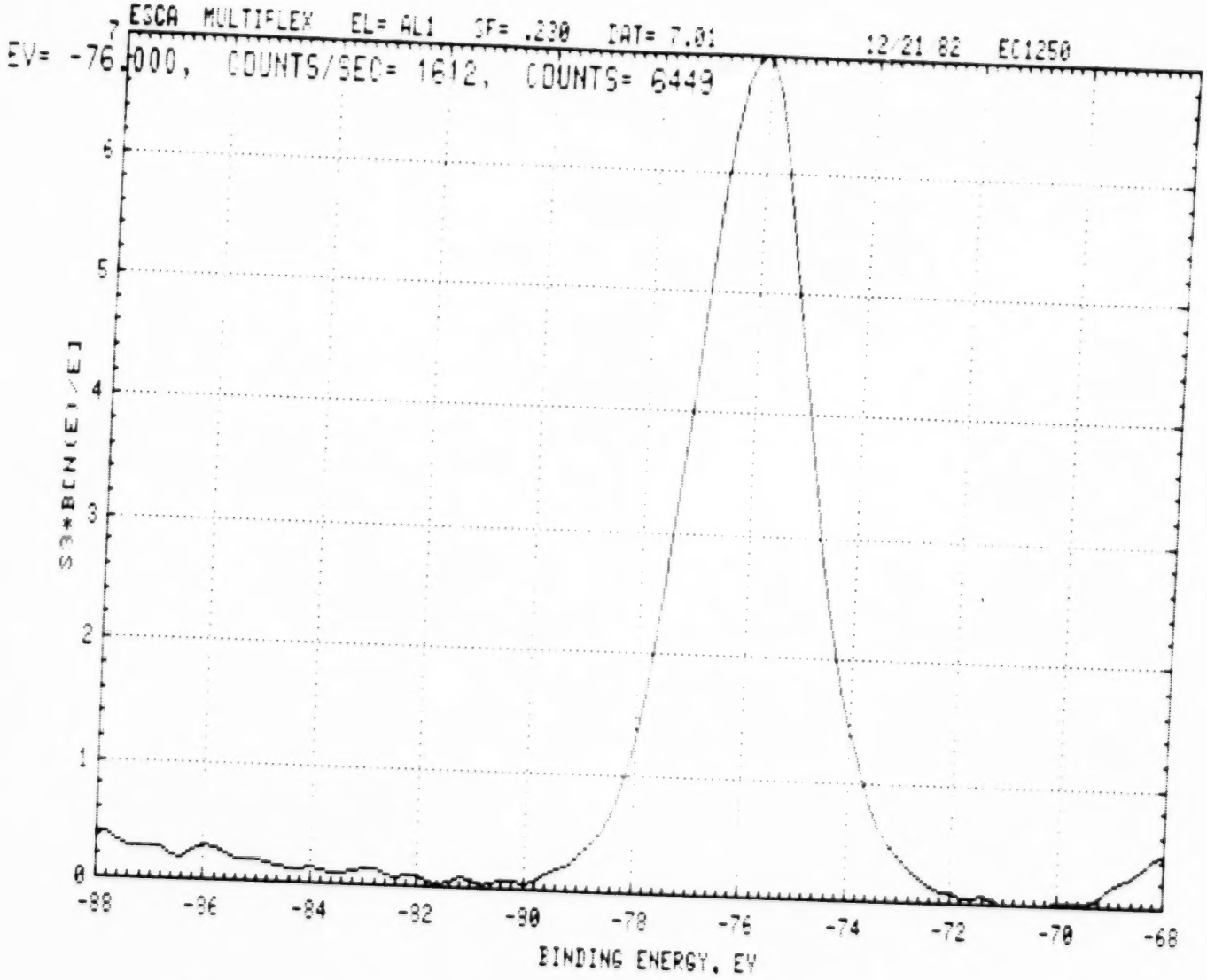
ESCA MULTIPLEX EL= AL1 SF= .230 IAT= 7.01 12/21 82 EC1250
EV= -76.000, COUNTS/SEC= 1612. COUNTS= 6449
S3*BCN(E)/E
BINDING ENERGY, EV
0
1
2
3
4
5
6
7
-88
-86
-84
-82
-80
-78
-76
-74
-72
-70
-68

Figure 22

POOR

QUALITY

ORIGINAL